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(54) Title: <b>PROCESS FOR PRODUCING A MULTI-LAYERED ARTICLE</b>			
(57) Abstract			
<p>The object of the present invention is to improve adhesion of PVDF to other materials and to provide processes for preparing multi-layered material containing the same. The first claimed process for laminating polyvinylidene fluoride resin onto another material which inherently do not adhere to the polyvinylidene fluoride resin is characterised in that an intermediate layer containing thermoplastic polyamide elastomer(s) and/or thermoplastic copolyester elastomer(s) is interposed between the polyvinylidene fluoride resin and another material. The second claimed process is characterised in that the PVDF resin is mixed with thermoplastic polyamide elastomer(s) and/or thermoplastic copolyester elastomer(s).</p>			

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## Specification

### Process for producing a multi-layered article

#### TECHNICAL FIELD

This invention relates to processes for bonding/laminating polyvinylidene fluoride resin to metal and/or polymer and/or resin which are not adhesive to the polyvinylidene fluoride resin.

The processes according to the present invention are applicable to lining of steel pipe, parts in chemical plants, marking film or the like.

#### PRIOR ART

Polyvinylidene fluoride resin (hereinafter, PVDF) possessing high weather- and chemical-resistances is utilised in many fields such as paint, electric or electronics parts, steel pipe liner, materials for chemical plants and staining and weather-resisting film. This resin, however, is difficult to be combined with other materials due to its poor adhesive property and its improvement is limited.

In order to overcome this problem, combinations with other polymers are proposed but are not satisfactory because there are few polymers that are compatible with or adhesive to PVDF or because inherent physical properties of PVDF are spoiled by such combination.

For example, polymethyl methacrylate resin (PMMA) is known as one of compatible resins with PVDF (JP-B-43-12012) but their mixture does not possess satisfactory flexibility because of the glass transition temperature of PMMA which is relatively higher than this one of PVDF. The other proposed combinations such as combinations with polycarbonate (JP-A-57-8244 et al), with polyethylene (JP-B-3-22901 et al), with functional denatured polyolefin (JP-A-62-57448 et al) and with polyimide (JP-A-2-308856) are not satisfactory because of poor compatibility.

#### PROBLEMS TO BE SOLVED BY THE INVENTION

An object of the present invention is to improve adhesion of PVDF to other materials and to provide processes for preparing multi-layered materials.

#### DISCLOSURE OF THE INVENTION

Thermoplastic polyamide elastomers (hereinafter, PAEs) and/or thermoplastic copolyester elastomers (hereinafter, TPEEs) possess adhesive and compatible properties to PVDF and their mixtures with PVDF also possess adhesive property to many other materials, and that these properties are useful in production of multi-layered structure of PVDF.

The present invention provides a first process for laminating polyvinylidene fluoride resin onto another material (A) which inherently does not

adhere to the polyvinylidene fluoride resin, characterised in that an intermediate layer containing more than 20 % by weight of thermoplastic polyamide elastomer(s) and/or thermoplastic copolyester elastomer(s) is interposed between the polyvinylidene fluoride resin and the other material (A), the  
5 intermediate layer may be made of thermoplastic polyamide elastomer(s) and/or thermoplastic copolyester elastomer(s).

The present invention provides a second process for laminating polyvinylidene fluoride resin onto another material (A) which inherently does not adhere to the polyvinylidene fluoride resin, characterised in that 10 to 100  
10 parts by weight of thermoplastic polyamide elastomer(s) and/or thermoplastic copolyester elastomer(s) are mixed with 100 parts by weight of polyvinylidene fluoride resin.

PVDF can be prepared by usual polymerisation technique such as emulsion polymerisation or suspension polymerisation and possess preferably  
15 a melt flow rate (MFR) of 0.01 to 500 g/10 min (230 °C under 2.16 kg).

PVDF is not limited to homopolymer of vinylidene fluoride but can be copolymers with copolymerizable monomers provided that the proportion of vinylidene fluoride in the copolymer is higher than 50 % by weight. Copolymerizable monomers may be tetrafluoroethylene, hexafluoropropylene,  
20 trifluoroethylene, chlorotrifluoroethylene, vinylidene fluoride and their combinations.

The materials (A) which inherently do not adhere to the polyvinylidene fluoride resin can be any materials including thermoplastic resins, thermosetting resins, rubber, metal, glass, ceramics, woods or their  
25 combinations.

The thermoplastic resins include polyvinyl chloride (PVC), polyvinyl chloride denatured with acryl, ethylene-vinyl chloride copolymer, ethylene-vinyl acetate-vinyl chloride copolymer, EVA resin, polyethylene, polypropylene, ethylene- $\alpha$ -olefin copolymer, olefin-vinyl alcohol copolymer, polystyrene, ABS  
30 resin, methacryl-styrene copolymer, polyurethane, polyamide (such as PA-6,6, PA-6, PA-12, PA-11, PA-4,6, PA-12,12, reinforced polyamide), polybutylene terephthalate, polyethylene terephthalate, aromatic polyesters, polyallylate, polycarbonate, polyphenylene ether, polyphenylene sulfide, polyether ketone, polyetheretherketone, polyethersulfone, polyetherimide, polysulfone,  
35 polyacetal, polyimide, cellulose plastics, polyvinyl alcohol and thermoplastic elastomers. In case of polyolefinic or polystyrenic resins, the adhesion to PVDF

can be improved by copolymerizing with at least a polar monomer -such as maleic anhydride- at a proportion of 0. 1 to 10 % by weight.

The thermosetting resins may be polyurethane resin, epoxy resin, phenols resin, alkyd resin, urea resin, melamine resin, benzoguanamine resin, bismaleimide resin and unsaturated polyester resin.

Metal as the material (A) can be iron, stainless, aluminium, copper, nickel, chromium, titanium, metallic alloys.

The PAEs according to the present invention are segmented block copolymers -the hard blocks consisting of aliphatic polyamides, the soft segments of aliphatic polyethers. Both segments are linked by ester or amide groups.

The amount of polyether moiety in the PAEs is preferably 30 to 80 % by weight. Outside this range, adhesive property and/or mechanical properties are spoiled.

The poly(oxyalkylene) chain (a) may be poly(oxyethylene), poly(oxy-1, 2- or 1, 3-propyl), poly(oxytetramethylene), poly(oxy hexamethylene), block or random copolymer of ethyleneoxide and propyleneoxide and block or random copolymer of ethyleneoxide and tetrahydrofuran. Preferably, their alkylene has a carbon number of 2 to 4 and terminal group is preferably hydroxyl or carboxyl group.

The number average molecular weight of the polyoxyalkylene chain is 300 to 6,000, preferably 500 to 4,000.

The polyamide units issue from aminocarboxylic acids having a carbon number generally higher than 6 and/or lactams and/or salts of diamine having a carbon number generally higher than 6 and dicarboxylic acids. Aminocarboxylic acids may be 6-aminocaproic acid, 8-aminocaprylic acid,  $\omega$ -aminopelargonic acid, 11-aminoundecanoic acid and 12-aminododecanoic acid. Lactams may be caprolactam, enantholactam, capryllactam and lauro lactam. Salts may be salt of hexamethylenediamine and adipic acid, hexamethylenediamine and sebacic acid, hexamethylenediamine and isophthalic acid, undecamethylenediamine and adipic acid, 4, 4-diamino cyclohexylmethane and dodecanedioic acid or the like. Among all the monomers listed above, 11-aminoundecanoic acid, 12-aminododecanoic acid, caprolactam, lauro lactam and salts of hexamethylenediamine and adipic acid or salts of hexamethylenediamine and sebacic acid are advantageously used. The polyamide units can be used in combination of more than two compounds.

Ester bonds which link hard and soft segments derive from dicarboxylic acids having generally a carbon number of 4 to 20 and can be (cyclo)aliphatic and/or aromatic; among the dicarboxylic acids, we can cite terephthalic acid, isophthalic acid, 1,4-naphthalenedicarboxylic acid, diphenyl dicarboxylic acid, 5 diphenoxyethane dicarboxylic acid, diphenyl ether dicarboxylic acid, diphenylsulfone dicarboxylic acid and sodium 3-sulfone isophthalate; cyclohexane dicarboxylic acid, dicyclohexyl dicarboxylic acid, decalin dicarboxylic acid, norbornane dicarboxylic acid and adamantane dicarboxylic acid; succinic acid, oxalic acid, adipic acid, sebacic acid and dodecanedioic 10 acid. Among these acids, adipic acid, sebacic acid and dodecanedioic acid are advantageously used.

When the link between the polyamide and the polyether moieties is an amide group, polyethers with amino end groups are used.

Polymerisation of PAEs can be effected by known process described in 15 JP-B-56-45419 and JP-1-46528 but is not limited thereto.

The thermoplastic copolyester elastomers according to the present invention are segmented block copolymers, consisting of repeating, high-melting, rigid "hard" blocks and amorphous, flexible "soft" blocks which have a very low glass transition temperature. They are typically produced by 20 condensation of an aromatic dicarboxylic acid or ester with a low molecular mass aliphatic diol and a polyalkylene ether glycol (molecular mass generally inferior to 4,000. Reaction of the aromatic dicarboxylic acid with the diol leads to the crystalline hard segment phase, while the soft segment is the product of the diacid (or diester) and the long-chain glycol. Among common raw materials, 25 we can cite iso- and terephthalic acids, dimethylterephthalate, butyleneterephthalate, butyleneterephthalate/ isophthalate, ethyleneterephthalate and butylene naphthalate, 2,6-naphthalenedicarboxylic acid as dicarboxylic acids, polypropylene and/or glycols, polytetramethyleneoxide as polyoxyalkylenes and 1,4-butane diol and ethylene glycol as short-chain diols.

30 The thermoplastic copolyester elastomers have generally a melt flow rate (MFR) of 0.1 to 50, preferably 0.5 to 20 at 200 °C under a load of 2.16 kg.

The poly(oxyalkylene) (a) chain may be poly(oxyethylene), poly(oxy-1, 2- or 1, 3-propyl), poly(oxytetramethylene), poly(oxy hexamethylene), block or random copolymer of ethyleneoxide and propyleneoxide and block or random 35 copolymer of ethyleneoxide and tetrahydrofuran. Preferably, their alkylene has a carbon number of 2 to 4 and terminal group is preferably hydroxyl or carboxyl

group. The number average molecular weight of the polyoxyalkylene chain is 300 to 6,000, preferably 500 to 4,000.

The polymer (b) of oxycarboxylic acid having a carbon number generally higher than 6 or dihydroxy compound having a carbon number higher than 2 and dicarboxylic acid having a carbon number generally higher than 6 may be p-oxybenzoic acid, p-hydroxyethoxybenzoic acid, oxynaphtoic acid, hydroxyethoxynaphtoic acid, ethyleneglycol, trimethyleneglycol, tetramethylene glycol, hexamethylene glycol, cyclohexane dimethanol, terephthalic acid, isophthalic acid, diphenyl dicarboxylic acid, diphenyl ketone dicarboxylic acid, diphenoxyethane dicarboxylic acid, naphthalene dicarboxylic acid or their combinations. Among them, butyleneterephthalate, butyleneterephthalate/isophthalate, ethyleneterephthalate and butylene naphthalate are advantageously used. The component (b) can be used in combination of more than two.

A weight ratio of (a) / (b) in the TPEE is 20/80 to 90/10, preferably 40/60 to 80/20.

In the first claimed process, PAE(s) and/or TPEE(s) are used in an adhesive intermediate layer (between the PVDF resin and the non-adhesive material A) as they are or in a mixture with other resins, such as PVDF. In case of a mixture, the proportion of PAE(s) and/or TPEE(s) in the said mixture is preferably higher than 20 % by weight, preferably 30 % by weight. If the proportion of PAE(s) and/or TPEE(s) is not higher than the value, satisfactory adhesion to other materials can not be expected.

The other resins of the intermediate layer include esters of polymethacrylic acid (such as PMMA), polyvinyl acetate, EVA resin, ethylene acrylate copolymer, polyolefins (polyethylene, polypropylene, ethylene- $\alpha$ -olefin copolymer and their denatured products modified with maleic anhydride), polybutyleneterephthalate, polyethyleneterephthalate, aromatic polyester, polyallylate, polycarbonate, polyacetal, methacrylate styrene copolymer, polyvinylchloride, polyurethane, polyamide (PA-6,6, PA-6, PA-12, PA-11, PA-4,6, PA-12,12, reinforced polyamide), elastomers and preferably PVDF.

The mixture with the other resins can be prepared by kneading components in a molten condition. Kneading can be done by any known technique without using any compatibility-improving agent to realise semi-micro dispersion. For example, the resin composition can be prepared in any known kneader such as Banbury mixer, rollers, single- or double-screw extruder at 100 to 300 °C, preferably 150 to 260 °C.

In the second claimed process the PVDF resin is mixed with PAE(s) and/or TPEE(s). PAE(s) and/or TPEE(s) are preferably used in a range of 10 to 100 parts by weight, preferably 20 to 60 parts, to 100 parts by weight of PVDF. If the proportion of PAE(s) and/or TPEE(s) is not higher than the lower limit, no improvement in adhesion is expected, while excess proportion of PAE(s) and/or TPEE(s) spoil inherent properties of PVDF (resistances to chemicals and weather).

The multi-layered articles according to the present invention are not limited to special products but include any molded articles including those produced by extrusion (film, sheet, plate, pipe, rod, profile, strand, monofilament, fiber), by injection moulding and compression moulding. The processes for producing multi-layered articles according to the present invention are applicable to a variety of molded articles and can be used advantageously as parts of instruments or agriculture film in which chemically inertness is required in the field of chemical, pharmaceutical and food industries, construction materials and agriculture film in which weather resistance for long time is required.

The resins and resin compositions according to the present invention i-e those of PVDF, of the intermediate layer mixture and the material (A) can contain know additives such as antioxidant, anti-pyrolysis agent, UV absorbent, anti-hydrolysis agent, colorant (dye, pigment), additives for adhesive and tackifier.

Lamination of the multi-layered articles can be done by any know technique such as calendering, co-extrusion, co-lamination, insert moulding, fluidized bed coating, dipping, spraying and coating.

#### EXAMPLES ACCORDING TO THE FIRST PROCESS

Melt Flow Rate (MFR) of PVDFs was determined at 230 °C under a load of 2.16 kg, MFR of TPEE was determined at 200 °C under a load of 2.16 kg and were expressed in term of g/10 min. The viscosity of PAEs was calculated from a solution viscosity of 0.5 % o-chlorophenol solution of polymer at 25 °C. The proportions of monomers are indicated by weight. Following polymers were used in Examples 1 to 5 and comparative Examples 1 to 4 :

- PVDF-1: homopolymer of PVDF 100 %, MFR = 20
- PVDF-2: copolymer of PVDF and hexafluoropropylene (5%), MFR = 8
- PVDF-3: copolymer of PVDF and trichlorofluoroethylene (9%), MFR = 7



PAE-1: a product between PA-6 having carboxylic acid end-groups derived from adipic acid and polyethyleneoxide having the number average molecular weight of 2,000 (proportions of 1/1). Relative viscosity = 1.8

5 PAE-2: a product between PA-12 having carboxylic acid end groups with dodecanoic diacid and polyethyleneoxide having the number average molecular weight of 2,000 (proportions of 1/1). Relative viscosity = 2.0

10 PAE-3: a product between the same PA-12 as above and polyethyleneoxide having the number average molecular weight of 1,000 (proportions of 1/1). Relative viscosity = 1.9

#### Test of adhesion

A film of PVDF was laminated on a plate or film (5 x 5 mm) and the laminated plate or film was sandwiched between two adhesive tapes. The  
15 condition of PVDF film was observed after the tapes were peeled off.

In Examples 1 and 2, three extruders (A, B, C) were used to feed three molten resins to a cross-head for producing a three-layered structure.

Extruder A (Length/Diameter = 20) for extruding the material A had a screw of compression ratio of 2.

20 Extruder B (L/D = 20) for extruding an adhesive layer B had a screw of compression ratio of 4.

Extruder C (L/D = 15) for extruding PVDF had a screw of compression ratio of 3.5.

Heating temperature was adjusted according to resins used.

25 The cross-head had three inlet ports, a flow divider and one outlet port. The resins of material A, of the adhesive intermediate layer and of PVDF were supplied to respective inlet ports to produce a three-layered composite at the outlet port. The three resins were fed in such a manner that the three-layered composite has a layer of about 0.25 mm for the material A and two layers of the  
30 adhesive and PVDF having each a thickness of 0.1 mm.

In Example 5 and comparative Example 2, two extruders B, C such as defined above were used to feed two molten resins to a cross-head for producing a two-layered structure.

The cross-head had two inlet ports, a flow divider and one outlet port.  
35 The adhesive and PVDF were supplied to respective inlet ports to produce a two layered composite at the outlet port. Two resins were fed in such a manner

that the two-layered composite has two layers : adhesiv / PVDF having a thickn ss of 0.1 mm ach.

#### Example 1

5 A three-layered sheet was produced by a coextruder by using polyamide-12 sold by Elf Atochem under denomination RILSAN® AESN-O-P40-TL as the material A, PAE-1 as adhesive intermediate layer, and PVDF-1 as PVDF resin.

The three layers were bonded firmly and no peeling was observed after the peeling test was repeated for 20 times. The sheet was flexible and was  
10 resistant to solutions of sulfuric acid and chromic acid.

#### Example 2

A three-layered sheet was produced by a coextruder by using polypropylene denatured with maleic anhydride sold by Elf Atochem under denomination OREVAC® PPFT, whose maleic anhydride weight contents is  
15 0.3 % as material (A), PAE-1 as adhesive intermediate layer, and PVDF-2 as PVDF resin.

The three layers were bonded firmly and no peeling was observed after the peeling test was repeated for 20 times.

#### Example 3

20 Procedure of Example 1 was repeated but the adhesive layer was replaced by a mixture of 100 parts by weight of PVDF-1 and 40 % by weight of PAE-1. The result was the same as in Example 1.

#### Example 4

100 parts by weight of PVDF-1 and 50 parts by weight of PAE-3 were  
25 mixed in a blender and fed to an extruder of single screw having cylinder temperatures of 170 to 240 °C to produce a film for adhesive having a thickness of about 0.1 mm. PVDF-1 was extruded by another extruder having the same cylinder temperatures to produce a film of PVDF-1. These films were used in the following extrusion-lamination stage.

30 100 parts by weight of polyvinyl chloride resin having the degree of polymerisation of 800, 2 parts by weight of tin type stabiliser, 10 parts by weight of MBS resin and 3 parts by weight of epoxidized soybean oil were kneaded in a roll at 170 °C and was passed through a calender roller to produce a polyvinyl chloride film of 0.3 mm thick, whil the PVDF-1 film and the  
35 polyvinyl chloride film were laminat d onto the polyvinyl chloride film to produce a three-layered film of polyvinyl chloride/adhesive/PVDF.

The three layers were bonded firmly and no peeling was observed after the peeling test was repeated for 20 times.

#### Example 5

A two-layered film was produced by using PVDF-3 and PAE-2. The extruders B and C such as defined above were heated at 150 to 220 °C and 160 to 230 °C respectively.

The resulting two-layered film was laminated on a steel plate of 0.2 mm thick at 220 °C in such a manner that the adhesive layer contacts with the steel plate.

The two-layered film was bonded firmly to the steel plate and no peeling was observed after the peeling test was repeated for 10 times. No change was observed on a surface of the PVDF layer which was exposed to 2N sulfuric acid solution at 50 °C for 2 months.

#### Comparative Example 1

Example 3 was repeated to produce a three-layered sheet but PAE-1 was replaced by polymethylmethacrylate. Adhesion at interlayers was poor so that peeling occurred at the fifth peeling test by adhesive tapes.

#### Comparative Example 2

A two-layered film was produced by using polypropylene denatured with maleic anhydride (OREVAC® PPFT) and PVDF-2. The extruders B and C were heated at 170 to 230 °C. Adhesion of the two layers was poor so that peeling occurred at the third peeling test by adhesive tapes.

#### Comparative Example 3

Example 4 was repeated but no intermediate layer was used. A two-layered sheet of PVDF-1 and of the same polyvinyl chloride resin as this one of Example 4 was produced by extrusion-lamination. Adhesion of the two layers was poor so that peeling occurred at the forth peeling test by adhesive tapes.

#### Comparative Example 4

Example 5 was repeated but no intermediate layer was used. A PVDF film was laminated onto a steel plate of 0.2 mm thick by the same process as in Example 4. Adhesion of the two layers was so poor that the PVDF layer peeled at the first peeling test by adhesive tapes.

Following polymers were used in Examples 6 to 9 and comparative Examples 5 to 8 :

PVDF-4 : homopolymer of PVDF 100 %, MFR = 2

PVDF-5 : copolymer of PVDF and hexafluoropropylene (11%), MFR =

PVDF-6 : copolymer of PVDF and trichlorofluoroethylene (15%), MFR = 0.9

TPEE-1 : a reaction product between butyleneterephthalate and polyoxytetramethyleneglycol having the number average molecular weight of 2,000 (proportions of 1/1). MFR = 8

TPEE-2 : a reaction product between a mixture of butyleneterephthalate/isophthalate (75/25) and polyoxy tetramethyleneglycol having the number average molecular weight of 2,000 (proportions of 1/2). MFR = 7

The adhesion test conditions are the same than those disclosed above.

In Examples 6 and 7, three extruders A, B, C such as defined above were used to feed three molten resins to a cross-head for producing a three-layered structure.

Heating temperature was adjusted according to resins used.

The cross-head has three inlet ports, a flow divider and one outlet port. The material, the intermediate layer and PVDF were supplied to respective inlet ports to produce a three-layered composite at the outlet port. The three resins were fed in such a manner that the three-layered composite has a layer of about 0.25 mm for the material (A) and the layers of the intermediate layer and PVDF having a thickness of 0.1 mm each.

In Examples 9 to 11 and comparative Examples 5, 8 and 5, two extruders B, C such as defined above were used to feed two molten resins to a cross-head for producing a two-layered structure.

The cross-head has two inlet ports, a flow divider and one outlet port. The intermediate layer mixture and PVDF were supplied to respective inlet ports to produce a two-layered composite at the outlet port. The two resins were fed in such a manner that the two-layered composite has two layers having a thickness of 0.1 mm each.

#### Example 6

A three-layered sheet was produced by a coextruder by using polyamide-12 sold by Elf Atochem under denomination RILSAN® AESN-O-P40-TL as the material, TPEE-1 as the intermediate layer, and PVDF-4 as PVDF resin. Cylinder temperatures of the extruders A, B, C were adjusted to 180 to 240 °C, 150 to 220 °C and 170 to 230 °C respectively.

The three layers were bonded firmly and no peeling was observed after the peeling test was repeated for 20 times. The sheet was flexible and was resistant to solutions of sulfuric acid and chromic acid.

#### Example 7

5 Procedure of Example 6 was repeated but the intermediate layer's mixture was replaced by a mixture of 100 parts by weight of PVDF-4 and 50 % by weight of TPEE-1. The result was the same as Example 6.

#### Example 8

10 100 parts by weight of PVDF-4 and 100 parts by weight of TPEE-2 were mixed in a blender and fed to an extruder of single screw having cylinder temperatures of 170 to 240 °C to produce a film for adhesive having a thickness of about 0.1 mm. PVDF-4 was extruded by another extruder having the same cylinder temperatures to produce a film of PVDF-4. These films were used in following extrusion-lamination stage.

15 100 parts by weight of polyvinyl chloride resin having the degree of polymerisation of 800, 2 parts by weight of tin type stabiliser, 10 parts by weight of MBS resin and 3 parts by weight of epoxidized soybean oil were kneaded in a roll at 170 °C and was passed through a calender roller to produce a polyvinyl chloride film of 0.3 mm thick, while the PVDF-4 film and the  
20 polyvinyl chloride film were laminated onto the polyvinyl chloride film to produce a three-layered film of polyvinyl chloride/adhesive intermediate layer/PVDF.

The three layers were bonded firmly and no peeling was observed after the peeling test was repeated for 20 times.

#### Example 9

25 A two-layered film was produced by using PVDF-6 and TPEE-2. The extruders B and C were heated at 150 to 220 °C and 160 to 230 °C respectively. The resulting two-layered film was laminated onto a steel plate of 0.2 mm thick at 230 °C in such a manner that the adhesive intermediate layer  
30 contacts with the steel plate.

The two-layered film was bonded firmly to the steel plate and no peeling was observed after the peeling test was repeated for 10 times. No change was observed on a surface of the PVDF layer which was exposed to 2N-sulfuric acid solution at 50 °C for 2 months.

35 100 parts by weight of polymethylmethacrylate sold by Mitsubishi Rayon under denomination ACRYPET and 100 parts by weight of TPEE-1 were blended and fed to an extruder to produce pellets for the adhesive intermediate

layer. A two-layered film was prepared in the co-extruder by using the adhesive pellets and PVDF-1. The extruders were heated at 150 to 220 °C and 160 to 230 °C respectively. The resulting two-layered film was laminated onto a steel plate of 0.2 mm thick at 230 °C in such a manner that the adhesive intermediate layer contacts with the steel plate.

The two-layered film was bonded firmly to the steel plate and no peeling was observed after the peeling test was repeated for 10 times. No change was observed on a surface of the PVDF layer which was exposed to 2N-sulfuric acid solution at 50 °C for 2 months.

As material (A), a polymer alloy comprising 50 % by weight of polyphenylene ether and 50 % by weight of polystyrene sold by GE Plastics Co. under denomination Noryl® 731 was used to prepare a film of 0.2 mm thick. This film was laminated at 230 °C in such a manner that the adhesive intermediate layer layer contacts with the material (A).

The PVDF layer bonded to the material (A) so firmly that no peeling was observed after the peeling test was repeated for 20 times. No change was observed on a surface of the PVDF layer which was exposed to 2N-sulfuric acid solution at 50 °C for 2 months.

#### Comparative Example 5

A two-layered film was produced in the co-extruder by using polyamide-12 of Example 6 and PVDF-4. The extruders B and C were heated at 170 to 230 °C. The adhesion of the two layers was so poor that peeling occurred at the third peeling test by adhesive tapes.

#### Comparative Example 6

Example 6 was repeated to produce a three-layered sheet but TPEE-1 was replaced by polymethylmethacrylate. Adhesion at interlayers was so poor that peeling occurred at the fifth peeling test by adhesive tapes. Flexibility of this two-layered film was not as high as in Example 6.

#### Comparative Example 7

Example 8 was repeated but no intermediate layer was used. A two-layered sheet of PVDF-4 and of the same polyvinylchloride resin as Example 9 was produced by extrusion lamination. Adhesion of two layers was so poor that peeling occurred at the forth peeling test by adhesive tapes.

#### Comparative Example 8

Example 9 was repeated but TPEE-2 as adhesive intermediate layer was replaced by the same polymethylmethacrylate as Comparative Example 6. A PVDF-6 film was laminated onto a steel plate of 0.2 mm thick by the same

process as Example 9. Adhesion of the two layers was poor so that PVDF layer peeled at the forth peeling test by adhesiv tapes.

#### Comparative Example 9

5 The two-layered film of PVDF/PMMA prepared in Comparative Example 6 was laminated onto a sheet of Noryl® 731 having a thickness of 0.2 mm. Adhesion of the two layers was poor so that PVDF layer peeled at the second peeling test by adhesive tapes.

#### EXAMPLES ACCORDING TO THE SECOND PROCESS

10 The PVDFs and PAEs used in the following examples have the same features than some used in the examples relating to the first process.

#### Example 12

15 100 parts by weight of PVDF-1 pellets and 30 parts by weight of PAE-1 were mixed in a blender and the resulting mixture was fed to an extruder of single screw (cylinder temperature = 170 to 240 °C) to produce a film of about 0.1 mm thick.

20 100 parts by weight of polyvinyl chloride resin having the degree of polymerisation of 800, 2 parts by weight of tin type stabiliser, 10 parts by weight of MBS resin and 3 parts by weight of epoxydized soybean oil were kneaded in a roll and passed through a roller to produce a polyvinyl chloride film of 0.3 mm thick.

The PVDF film and the polyvinyl chloride film were laminated by rollers at 190 °C to produce a two-layered film.

The two layers were bonded firmly and no peeling was observed after 20 times of peeling test.

#### 25 Example 13

Procedure of Example 12 was repeated but PVDF-1 was replaced by PVDF-2 and the polyvinyl chloride film was replaced by a film of maleic anhydride denatured polypropylene whose maleic anhydride weight contents is 0.3 % sold by Elf Atochem under denomination OREVAC® PPFT.

30 The two layers of PVDF and polypropylene were bonded firmly and no peeling was observed after 20 times of peeling test.

#### Example 14

35 100 parts by weight of PVDF-1 pellets and 30 parts by weight of PAE-3 were mixed in a blender and the resulting mixture was fed to an extruder of single screw (cylinder temperature = 170 to 240 °C) to produce a film of about 0.1 mm thick.

The resulting film was laminated with a film of PA-12 having a thickness of 0.3 mm at 230 °C.

The resulting two layers were bonded firmly and no peeling was observed after 20 times of peeling test.

5        Example 15

100 parts by weight of PVDF-3 pellets and 40 parts by weight of PAE-2 were mixed in a blender and the resulting mixture was fed to an extruder of single screw (cylinder temperature = 170 to 240 °C) to produce a film of about 0.1 mm thick.

10        The resulting film of PVDF was laminated onto a stainless steel plate having a thickness of 0.3 mm at 200 °C.

The resulting two layers were bonded firmly and no peeling was observed after 5 times of peeling test.

Comparative Example 10

15        Pellets of PVDF-1 were rolled to produce a film of 0.1 mm. This film was laminated by a press with the same polyvinyl chloride film as in Example 12

The two layers separated at the third peeling test by adhesive tapes.

Comparative Example 11

Example 13 was repeated but PAE was not added to PVDF-2.

20        The two layers separated at the second peeling test by adhesive tapes.

Comparative Example 12

Example 14 was repeated but PAE was not added to PVDF-1.

The two layers separated at the second peeling test by adhesive tapes.

Comparative Example 13

25        Example 13 was repeated but PAE was not added to PVDF-3.

The two layers separated at the first peeling test by adhesive tapes.



## Claims

1. Process for laminating polyvinylidene fluoride resin onto another material (A) which inherently does not adhere to the polyvinylidene fluoride resin, characterised in that an intermediate layer comprising at least a thermoplastic polyamide elastomer and/or at least a thermoplastic copolyester elastomer and containing more than 20 % by weight of said thermoplastic polyamide and/or copolyester elastomer(s) is interposed between said polyvinylidene fluoride resin and said another material (A).

2. Process for laminating polyvinylidene fluoride resin onto another material (A) which inherently does not adhere to the polyvinylidene fluoride resin, characterised in that 10 to 100 parts by weight of thermoplastic polyamide elastomer(s) and/or thermoplastic copolyester elastomer(s) are mixed with 100 parts by weight of polyvinylidene fluoride resin.

3. Process according to claim 1 or 2, wherein said polyvinylidene fluoride resin is homo-polymer of polyvinylidene fluoride and/or copolymer containing more than 50 % by weight of polyvinylidene fluoride monomer.

4. Process according to claims 1 to 3, wherein the content of polyether in thermoplastic polyamide elastomer is 30 to 80 % by weight and is preferably selected from polyethylene glycol, polypropylene glycol and polytetramethyleneglycol.

5. Process according to claims 1 to 4, wherein the content of polyether in thermoplastic copolyester elastomer is 40 to 80 % by weight and is preferably selected from polyethylene glycol, polypropylene glycol and polytetramethyleneglycol.

6. Process according to claims 1 to 5, wherein said another material is of thermoplastic and/or thermosetting resin and/or metal

7. Multi-layered-articles comprising :

- \* a layer of a material (A) which inherently does not adhere to the polyvinylidene fluoride resin,

- \* a PVDF layer

- \* and an adhesive intermediate layer comprising at least a thermoplastic polyamide elastomer and/or at least a thermoplastic copolyester elastomer is and containing more than 20 % by weight of said thermoplastic polyamide and/or copolyester elastomer(s) is interposed between said polyvinylidene fluoride resin and said another material (A).

**8. Multi-layered-articles comprising :**

- \* a layer of a material (A) which inherently do s not adhere to the polyvinylidene fluoride resin,
- \* a PVDF- based layer in which 10 to 100 parts by weight of thermoplastic polyamide elastomer(s) and/or thermoplastic copolyester elastomer(s) are mixed with 100 parts by weight of polyvinylidene fluoride resin.

9. Composition based on PVDF, characterised in that it comprises at least a thermoplastic polyamide elastomer and/or at least a thermoplastic copolyester elastomer.

10. Composition according to claim 9 comprising 10 to 100 parts of thermoplastic polyamide elastomer(s) and/or thermoplastic copolyester elastomer(s) for 100 parts by weight of polyvinylidene fluoride resin.

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# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/cP 95/04696

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B32B27/08 C08L27/16 F16L9/133

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B32B C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 450 994 (ATOCHEM ELF SA) 9 October 1991 see claim 1 ---	2,3,6, 8-10
X	DATABASE WPI Section Ch, Week 9327 Derwent Publications Ltd., London, GB; Class A14, AN 93-216246 & JP,A,05 138 820 (DENKI KAGAKU KOGYO KK) , 8 June 1993 see abstract ---	2,3,6, 8-10
X	EP,A,0 271 068 (MITSUBISHI PETROCHEMICAL CO) 15 June 1988 see page 10, line 17 - page 11, line 24; claims 1,2,7,8 --- -/--	2,3,6, 8-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*&\* document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 95/04696

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	<p>EP,A,0 386 630 (ROEHM GMBH) 12 September  1990  see claims</p> <p style="text-align: center;">---</p>	9
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